Final Technical Report

on

Investigation of Selective Non-Catalytic Processes for In-Situ Reduction of NO_x and CO Emissions from Marine Gas Turbines and Diesel Engines

Prepared for

Office of Naval Research

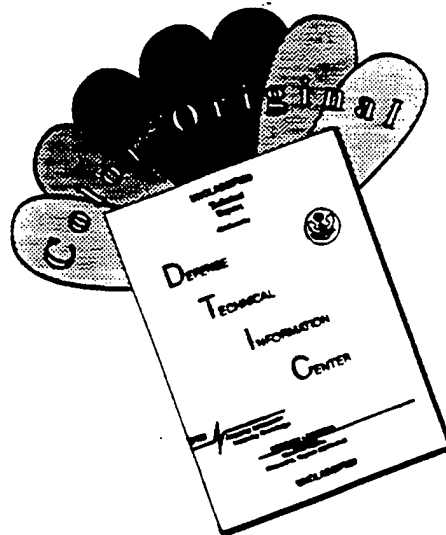For the Period

1 April 1994 to 31 March 1997

Submitted by

Craig T. Bowman and Ronald K. Hanson

HIGH TEMPERATURE GASDYNAMICS LABORATORY
Mechanical Engineering Department
Stanford University

19970515 050

DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF COLOR PAGES WHICH DO NOT REPRODUCE LEGIBLY ON BLACK AND WHITE MICROFICHE.

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (*Leave Blank*)	2. REPORT DATE 15 May 1997	3. REPORT TYPE AND DATES COVERED Final Technical 1 April 1994 to 31 March 1997

4. TITLE AND SUBTITLE
Investigation of Selective Non-Catalytic Processes for In-Situ Reduction of NO_x and CO Emissions from Marine Gas Turbines and Diesel Engines

5. FUNDING NUMBERS

6. AUTHORS
Craig T. Bowman
Ronald K. Hanson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Stanford University
Mechanical Engineering Department
Thermosciences Division
Stanford, CA 94305-3032

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5669

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The effectiveness of selective non-catalytic reduction (SNCR) gas-phase reaction processes for NO_x removal from combustion products was investigated at elevated pressures in a combined experimental and modeling program. Experiments were conducted in a high-pressure flow reactor, and simulations were carried out using a state-of-the-art chemical model. The experiments focused on the reduction of NO by injection of NH_3 into the combustion products. NO reductions as a function of temperature were measured for pressures of one and two atmospheres. The observed NO reductions were well-predicted by the chemical model. Additional simulations at higher pressures indicate that the temperature window for NO_x removal widens as pressure increases.

In addition, a project was carried out to develop compact, robust solid-state sensors for pollutant species for use in control systems for reduction of pollutant emissions. The sensor concept is based on integrated circuit fabrication technologies that allow the integration of a metal oxide sensor with associated circuitry on a single chip. A sensor for NO_x was designed, fabricated and tested. The sensor showed good sensitivity and selectivity for NO_x in lean combustion products.

14. SUBJECT TERMS
pollution control, NO_x emissions, electrochemical sensors

15. NUMBER OF PAGES
11

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-1
298-102

Table of Contents

1.0 Summary

The effectiveness of selective non-catalytic (SNCR) gas-phase reaction processes for NO_x removal from combustion products at elevated pressures was investigated in a combined experimental and modeling research program. Calculations using existing chemical models for SNCR indicate that the temperature window for NO_x removal by SNCR widens as pressure increases, resulting in NO_x removal at higher temperatures than at ambient pressure. The calculations also show a significant reduction in the reaction time scale with increasing pressure. These observations suggest the possibility of utilizing SNCR for reducing NO_x emissions from marine gas turbines and Diesel engines by direct injection of a reductant species into the combustion chamber, possibly as a fuel additive. Initial experiments were carried out at atmospheric pressure to allow comparison with previous measurements in order to verify the experimental approach. Following these validation tests, experiments were conducted at elevated pressures. Results from these tests, confirm the model predictions that the SNCR window for NO_x removal widens as the pressure increases. In addition, a project was initiated, to develop compact, robust, solid-state microsensors for pollutant species for use in control systems for reduction of pollutant emissions. The sensor concept is based on integrated circuit fabrication technology that allows the integration of a metal-oxide sensor with associated electronic circuitry on a single chip. Initial efforts focused on development of a sensor for NO_x.

2.0 Introduction

Currently available combustion modifications to reduce NO_x emissions from power-generating gas turbines and Diesel engines cannot meet existing stringent NO_x emissions standards. For this reason, post-combustion methods for NO_x removal from combustion products have been developed that are applicable to both gas turbines and Diesel engines. Some of these methods are based on injection of a nitrogen-containing reductant into the combustion products. The reductant initiates a reaction sequence leading to NO_x removal. The NO_x-removal process may take place entirely in the gas-phase (in a process termed Selective Non-Catalytic Reduction, SNCR), or it may take place partly or entirely on the surface of a catalyst (in a process termed Selective Catalytic Reduction, SCR). At atmospheric pressure, NO_x removal occurs within a narrow temperature window centered about 1250K for SNCR and centered about 600K for SCR. Typical exhaust gas temperatures in gas turbines are too low to utilize SNCR for NO_x removal from the exhaust gas, so that only the more complex and expensive SCR technique may be used. Exhaust temperatures in some Diesel engines are sufficiently high so that either SNCR or SCR may be used for NO_x emissions reduction; but, frequently, an additive or an external heat source is employed to improve the performance of SNCR.

There are several disadvantages in using conventional SNCR or SCR for NO_x emissions reductions in naval powerplants. First, the reductant must be carried on board the vessel in a separate storage tank. Second, the exhaust ducting from the engine must be modified to accommodate reductant injection and possibly a catalyst bed, resulting in an increased

footprint for the overall powerplant. Third, an additional control system for the process is required.

Because of the high NO$_x$-removal efficiency and relative simplicity of SNCR, the possibility of applying SNCR to gas turbines and Diesel engines by direct injection of a reductant into the combustion chamber, where the pressures and temperatures are higher, should be investigated. If significant NO$_x$ removal can be obtained for these conditions, then it may be possible to include the NO$_x$-removing species as a fuel additive, thereby simplifying the application of the process to existing powerplants.

Some strategies to reduce NO$_x$ emissions, for example, partial premixing (Gore et al., 1995), flow forcing (Sivasegaram and Whitelaw, 1995) or chemical or plasma after-treatment processes (Gundersen et al., 1995) require a control system to achieve maximum effectiveness. A major component of such control systems is a sensor for NO$_x$ in the exhaust gas. The signal from this sensor is used as feedback in the control system. Existing sensors for pollutant species, such as NO$_x$ or CO, lack sensitivity and time response, and they often exhibit poor selectivity to the desired pollutant species. In addition, these sensors are expensive. Hence, there is a need for development of compact, robust, sensitive and inexpensive sensors for pollutant species for use in control systems for emissions reduction and compliance monitoring.

3.0 Background

3.1 Emissions Reduction by SNCR

Available chemical models for SNCR (Glarborg et al., 1994; Bowman, 1997) have been used to explore the effects of pressure, temperature, exhaust gas composition, reaction time-scale and reductant type on NO$_x$-removal efficiency. Figure 1 shows the principal reaction pathways for NO removal for several common SNCR additives. In all cases the process requires generation of radical species, usually OH, H, or O that drive the overall process. NO removal occurs by reaction of NO with a nitrogen-containing radical formed from the injected compound to produce either N$_2$ or N$_2$O. The N$_2$O may subsequently react to form N$_2$ or it may be emitted from the system. At sufficiently high temperatures, the injected nitrogen compound oxidizes to produce additional NO. At low temperatures, there is insufficient radical generation to sustain the process. Hence, there is a temperature window where SNCR is effective in reducing NO in the combustion products. Some of the NO in the combustion products may be converted to NO$_2$ via reaction with the HO$_2$ radical that forms at lower temperatures.
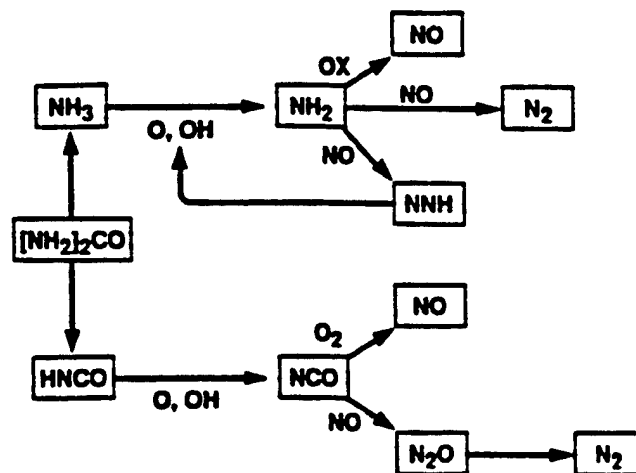
Fig. 1 Reaction path diagram illustrating the major steps in gas-phase
NO removal by reaction with ammonia, isocyanic acid and
urea (Bowman, 1997).

Figures 2 – 5 show typical results from simulations for two commonly used nitrogen-containing reductants, ammonia (NH_3) and isocyanic acid (HNCO). At one atmosphere pressure, the calculated NO_x-removal temperature window for NH_3 extends from 1200K – 1400K, Fig. 1. With increasing pressure, the calculated width of the NO_x-removal temperature window increases. At 20 atmospheres pressure, the window extends from 1200K – 1550K. Also shown on Fig. 1 is a typical operating line of a marine gas turbine, indicating the possibility of significant reductions of NO_x emissions from gas turbines by in-situ SNCR.
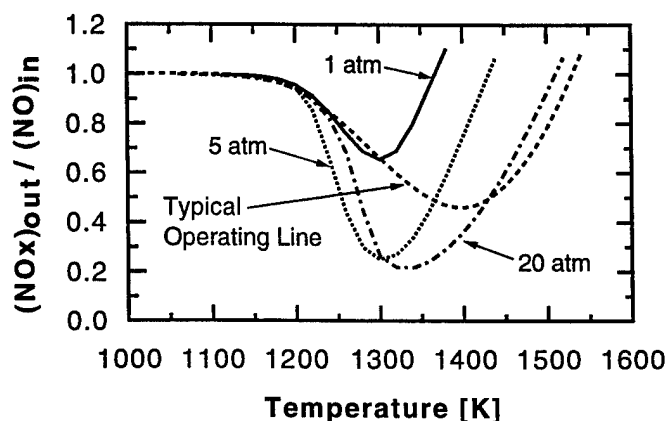

Fig. 2 Calculated reduction in NO_x ($NO + NO_2$) in combustion
products as a function of temperature and pressure for
added NH_3. Initial $NO = 250$ ppm; initial $NH_3 = 500$ ppm;
$O_2 = 10\%$; reaction time = 10 ms. A typical gas turbine
operating line is shown on the plot.

3

Smith and Caton (1995) have reported measurements of NO_x removal with NH_3 injection where total NO_x emissions were found to increase slightly with increasing pressure due to conversion of $NO \rightarrow NO_2$. However, recent measurements by Kjaeraard et al. (1996) show no significant NO_2 emissions at pressures up to 5 atmospheres, and a widening NO_x removal window with increasing pressures, in agreement with the model results, Fig. 3.
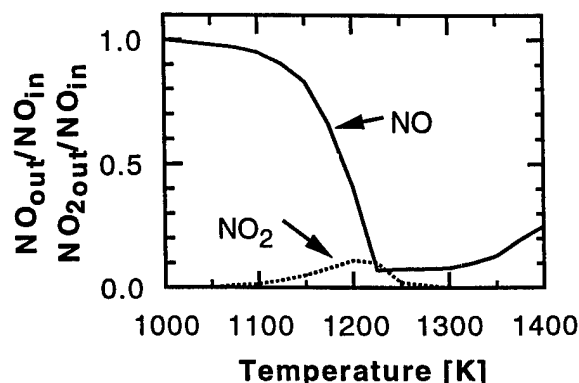

Fig. 3 Calculated NO and NO_2 in combustion products as a function of
temperature for added NH_3 and a pressure of 20 atmospheres.
Initial NO = 225 ppm; initial NH_3 = 385 ppm; O_2 = 5.1%; reaction
time = 100 ms.

Figure 4 compares the calculated NO-removal efficiencies for the two reductant types at a pressure of 20 atmospheres for two different exhaust O_2 levels. The location of the NO_x-removal temperature window and the NO_x-removal efficiency are strongly dependent on the molecular structure of the reductant species, but only weakly dependent on the O_2 levels . The differences in the temperature windows are the consequence of the different reaction mechanism for NH_3 and HNCO and are in qualitative agreement with the data of Smith and Caton (1995).
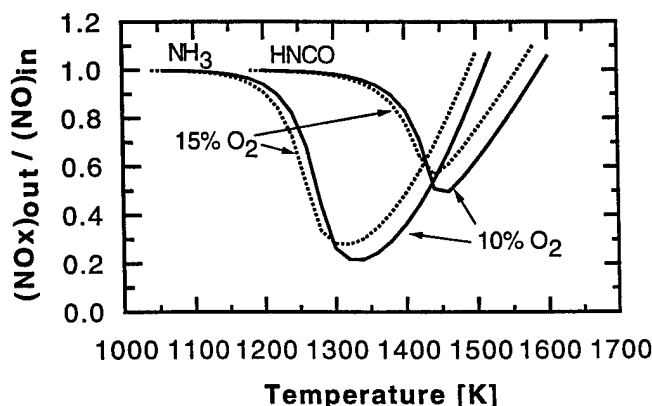

Fig. 4 Calculated reduction in NO_x in combustion products as a function of
temperature, reductant type and O_2 levels. Initial NO = 250 ppm; initial
reductant = 500 ppm; pressure = 20 atmospheres; reaction time = 10 ms.

4

An additional predicted benefit of the SNCR process, Fig. 5, is the consumption of a significant fraction of the residual CO in the combustion products, thereby reducing CO emissions, although there are no experimental data to support this model result.
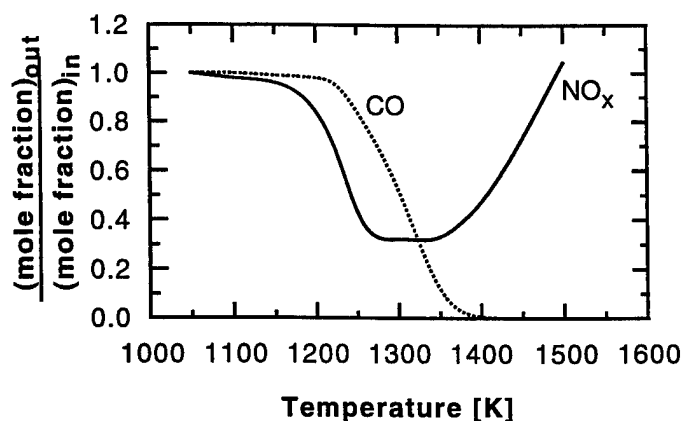

Fig. 5 Calculated reduction in NO_x and CO in combustion products as a function of temperature for added NH_3. Initial NO = 300 ppm; initial CO = 600 ppm; initial NH_3 = 600 ppm; O_2 = 15%; pressure = 20 atmospheres; reaction time = 10 ms.

3.2 Solid-State Pollutant Sensors

Pollutant sensors play critical roles in control systems for emissions reduction and in compliance monitoring. Of particular interest for control and monitoring of NO_x emissions is a sensor for NO_x. The standard method for measurement of NO_x in combustion gases is based on extractive probe sampling followed by on-line measurement of NO and NO_2 using either a chemiluminescence analyzer or non-dispersive optical analyzers. While quantitatively accurate and species specific, both of these analyzer types have a number of disadvantages, including high cost, the need for periodic calibration, a slow time response, and large size. Hence, there is a need for the development of inexpensive, compact, species specific sensors with rapid time response. Electrochemical transducers represent an attractive class of species sensor that only recently have begun to see application to measurement of regulated pollutants. Most of these sensors utilize thin films of metal oxides and work on resistive changes associated with adsorption of gas on the film. A particularly attractive approach is the combination of the metal oxide sensor with the electrical and electronic elements on a single chip using modern integrated circuit manufacturing techniques. This approach was followed in this phase of the present research effort in order to develop a microelectrochemical semiconductor metal oxide sensor for the measurement of nitrogen oxides in combustion exhaust gases.

5

4.0 Approach

4.1 Emissions Reduction by SNCR

Experiments to examine the dependence of NO_x removal by SNCR on pressure, temperature, reductant type, exhaust gas composition and reaction time were carried out in a high-pressure reactor, shown schematically in Fig. 6.
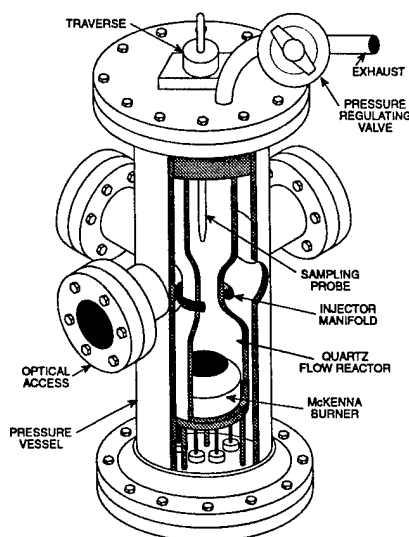

Fig. 6 Schematic diagram of the high-pressure reactor.

A pressure vessel, designed for operation at pressures up to 50 atmospheres, houses a plug flow reactor. The plug flow reactor was employed in the experiments as it allowed investigation of the widest range of temperatures, exhaust gas compositions, reaction times and reductant types. The hot gas source for the flow reactor is a premixed, laminar, flat flame burner. To achieve the desired ranges of exhaust gas composition and temperature, the burner is operated using lean CH_4-air mixtures. The nitrogen-containing reductant species, together with NO, is injected through six radial opposed jets located at the throat of a converging-diverging nozzle to achieve rapid mixing. The NO-removal efficiency depends somewhat on the O_2 level in the combustion products. To vary the O_2 levels in the combustion products, additional O_2 or N_2 is injected through the jets. A traversing gas sampling or temperature probe is located on the duct centerline. Product gas composition is determined using chemiluminescence, NDIR and ion analyzers. Stable product species measured included NO, NO_2, CO and the reductant to establish reductant slip.

Two nitrogen-containing reductants, NH_3 and HNCO, are of interest in order to determine the role of the reductant molecular structure on the NO_x-removal efficiency. These reductants were chosen because the NO-removing radical species (NH_2 or NCO) are representative of those that would be produced by likely fuel additives, because there is an extensive data base on these species at atmospheric pressure, and because chemical models

6

for the performance of these reductants have been developed. In the experiments reported here, only NH₃ was employed.

4.2 Solid-State Pollutant Sensors

This phase of the research program comprised two primary efforts: (1) design and fabrication of an integrated metal oxide sensor for NO_x in combustion gases and (2) testing of the sensor for sensitivity, selectivity, stability and time response in simulated combustion products.

The sensor design is based on the technology utilized in the design and fabrication of metal oxide semiconductors. A key feature in the sensor design is selection of the metal oxide film. The desirable characteristics of the film include excellent sensitivity and selectivity for the species of interest and good time response. The most commonly used metal oxide for microchemical sensors, SnO_2, shows excellent sensitivity to combustible gases, CO and NO_x. However, this broad-based sensitivity results in poor selectivity. The selectivity of SnO_2 to NO, can be marginally improved by doping with metals such as Ga, Al or In. The metal oxide adopted here is WO_3. Recent studies (Akiyama et al., 1993) have shown WO_3 to be both sensitive to and selective for NO_x. A typical transient response of WO_3 films to NO_x is shown in Fig. 7. There is a tradeoff between time response and sensitivity, and the sensor surface temperature plays a key role in this tradeoff. Hence, control of the sensor surface temperature is a critical feature of the sensor design.
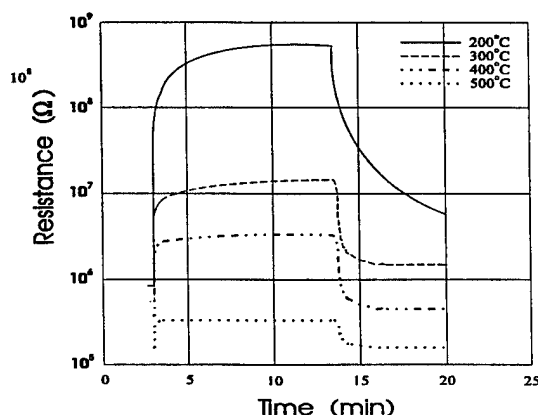

Fig. 7 Transient response of a WO_3 film to 200 ppm NO in air as a function of film temperature (Akiyama et al., 1993).

5.0 Results

5.1 Emission Reductions by SNCR

An initial experiment using NH₃ as a reductant was carried out in the flow reactor at atmospheric pressure to verify experimental procedures. The measured reductions of NO as a function of temperature are compared with model predictions in Fig. 8; the

conditions of this experiment are listed in the figure caption. Good agreement between the data and model results is observed. For the conditions of this experiment, measured NO_2 mole fractions were always below 2 ppm.

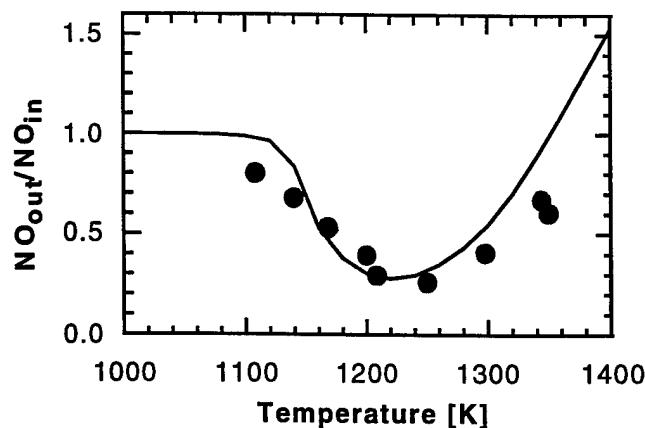Fig. 8 Comparison of measured and calculated NO removal from
combustion products for injected NH_3. Initial NO = 100 ppm;
initial NH_3 = 385 ppm; O_2 = 5.1%; H_2O = 7.3%; CO_2 = 3.6%;
balance = N_2; nominal reaction time = 100 ms; pressure = 1 atm.

Following completion of the atmospheric-pressure validation tests, experiments were conducted at a pressure of two atmospheres. Results from these experiments are shown in Fig. 9, together with the model predictions. Again, good agreement between the model results and data is observed. Similar to the atmospheric-pressure experiments, measured NO_2 mole fraction were below 2 ppm. Comparison the NO-removal efficiencies of Figs. 8 and 9, indicates a modest widening of the NO-removal window toward higher temperatures, in agreement with model predictions.
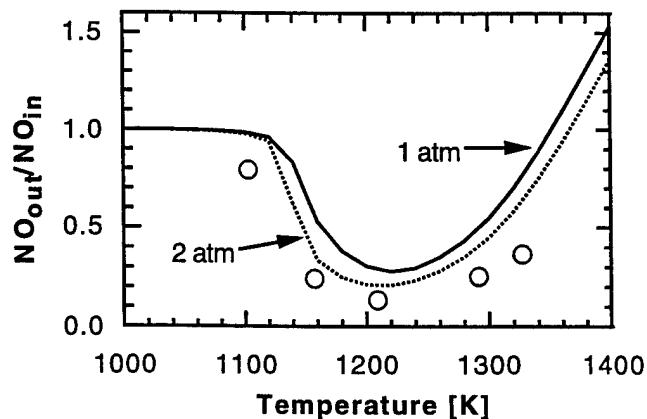

Fig. 9 Comparison of measured and calculated NO removal
from combustion products for injected NH_3. Conditions
identical to Fig. 8, except pressure = 2 atm. Solid line shows
model results for a pressure of 1 atm.

8

5.2 Solid-State Pollutant Sensor

A schematic diagram of the solid-state NO_x sensor design is shown in Fig. 10, and a photomicrograph of a fabricated sensor is shown in Fig. 11. The sensor is a thin tungsten oxide film on a sensor body that comprises aluminum electrodes, an aluminum temperature sensor and a PECVD (plasma enhanced chemical vapor deposition) polysilicon heating element. The integrated temperature sensor and heater maintain the film temperature at a prescribed level that is independent of the combustion gas temperature. The sensor body is suspended above a silicon substrate to provide good thermal insulation using four SiO_2 beams. The electrical connections to the heating element and sensor are routed over these beams.

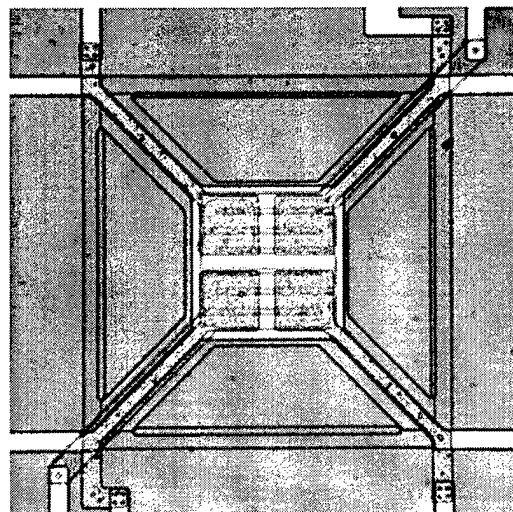Fig. 10 Cross-section of the solid-state microchemical NO_x sensor.

Fig. 11 Photomicrograph of the solid-state microchemical NO_x sensor.
The overall dimensions of the sensor are 200 μm x 200 μm.

The first stage of the sensor manufacturing, involving deposition of all films except the tungsten oxide film, was completed at a commercial foundry. The subsequent manufacturing steps, including etching to remove material under the sensor body, sputtering of the WO_3 film, and bonding were carried out in the Center for Integrated Systems at Stanford University.

Following fabrication, the sensor was tested in simulated combustion products to establish sensitivity, selectivity and time response. Preliminary tests with this sensor design shows excellent sensitivity for NO and NO_2.

6.0 References

Akiyama, M., Zhang, Z., Tamaki, J., Miura, N., Yamazoe, N. and Harada, T. (1993), Sensors and Actuators, B, **13-14**, 619.

Bowman, C. T. (1997), "Mechanism and Modeling of Gas-Phase Aftertreatment Methods for NO Removal from Combustion Products," *Physical and Chemical Aspects of Combustion: A Tribute to Irvin Glassman*, Gordon Breach (in press).

Glarborg, P., Dam-Johansen, K., Miller, J. A., Kee, R. J. and Coltrin, M. E. (1994), Int. J. Chem. Kinetics 26, 421.

Gore, J. P. (1995), "NO_x Reduction Using Lean Direct Injection in Naval Engines," Eighth ONR Propulsion Meeting Proceedings, pp. 1-9.

Gundersen, M., Puchkarev, V. and Roth, G. (1995) "Plasma Treatment of Diesel Exhausts," Eighth ONR Propulsion Meeting Proceedings, pp. 60-63.

Kjaergaard, K., Glarborg, P., Dam-Johansen and Miller, J. A. (1996), 26th Symp. (Int.) on Combustion, pp. 2067-2074.

Sivasegaram, S. and Whitelaw, J. H. (1995), "Control of Combustion and Emissions," Eighth ONR Propulsion Meeting Proceedings, pp. 10-20.

Smith, T. S. and Caton, J. (1995), Papers 95S-015 and 16, Joint Central and Western States Section and Mexican National Section of the Combustion Institute and American Flame Research Committee Meeting, San Antonio.